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**Using Molecular Transformations To Monitor *In Situ* Upgrading Operations In Oil Sands  
And Heavy Oil Reservoirs**

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**Summary**

Upgrading of heavy oil and oil sands under simulated high temperature thermal recovery reservoir conditions was conducted to evaluate mechanisms and sources of the produced light hydrocarbon compounds that directly affect oil fluid properties as well as the identification of geochemical proxies to monitor in situ upgrading operations. The main results suggest that the asphaltene fraction is the main source of the light hydrocarbons produced during the simulated upgrading process. The neoformation of novel compounds such as alkylanthracenes and alkylbenzothiophenes in our experiments and their observed formation in oils from current generation thermal recovery SAGD pilots suggests some molecular changes are suitable to monitor steaming effects under current thermal recovery conditions from analysis of produced oils, as well as monitoring more dramatic changes under high temperature insitu upgrading conditions.

**Introduction**

The world oil inventory is dominated by heavy oils and oil sand bitumens generated almost entirely by the process of biodegradation of conventional oil over geological timescales. These oils are difficult to produce and transport because of their high viscosity. Reservoir heating by steam or electricity and/or solvent injection to mobilize the oil is often essential in very heavy oil and oil sand recovery. During in-situ thermal recovery processes the injected steam heats the crude oil or bitumen and lowers its viscosity allowing it to flow. Viscosity reduction with increasing temperature is regarded as a proven mechanism for very heavy oil recovery since the viscosity decreases over several orders of magnitude when the temperature is raised to 200 °C. Heat from steam injection can also effect very minor changes in the chemical composition of the oil but employing catalysts in the reservoir and increasing temperatures above steam temperature during in-situ upgrading of heavy oil and bitumen may enable a more desirable product to be produced within a short timescale. However, there is currently no system established to monitor the chemical processes in-situ during thermal recovery or insitu upgrading where heat hydrogen, water, catalysts and oil all interact in a complex natural reactor. A detailed knowledge of the molecular transformation undergone by heavy oil and bitumen under in-reservoir thermal or catalytic processing allows the chemical composition of the produced oil to be used as a natural tracer to monitor the progression of the steam or upgrading front in the subsurface. The present study describes the changes caused by various reactions occurring during steam injection simulation. We look at the impact of heating oil sands with water under conditions that might

ensue in an in-situ process where heat is applied to the reservoir via superheated steam, electrical heating or in-situ combustion where water is present.

### Method

Heavy oil and oil sands core samples were processed under hydrous conditions up to 350°C for time periods of up to seven days using regular water. Pyrolysates were analyzed for bulk and molecular composition. For molecular investigation, the total hydrocarbon fractions were isolated following de-asphalting of the bitumen and heavy oil samples. GCMS analysis was performed on an Agilent 6890 N network gas chromatograph (GC) system, coupled to an Agilent 5975 XL MSD. The saturated hydrocarbons, aromatic hydrocarbons, resins and asphaltenes (SARA) content were determined by Thin Layer Chromatography, using an Iatroscan Mk 6S instrument equipped with a flame ionization detector.

### Results

The main results demonstrate that native oil sands bitumens are naturally characterized by a lack of n-alkane and isoprenoid alkane hydrocarbons and generate a relatively uniform pattern of n-alkanes up to C<sub>30</sub> and isoprenoid alkanes such as pristane and phytane, under high temperature simulated thermal recovery conditions (over 300°C, Figure 1). The generation of tricyclic condensed aromatic hydrocarbon molecules, some of which are not present, or are at very low concentration in the original oil sand, appear to be good indicators of the progress of thermal conversion. For instance, the production of alkylanthracenes follows pseudo apparent first-order kinetics allowing the calculation of pseudo rate constants (Figure 2). Such parameters can be used to track process oil temperature histories.

The evaluation of some molecular parameters traditionally used to monitor thermal stress in basin settings and also recently proposed as proxies for in reservoir process monitoring<sup>3</sup>, suggests that those parameters based on biomarker ratios are probably suitable to be used as proxies for thermal conversion in procedures with temperatures below approximately 300°C. Under the most extreme experimental conditions (350°C) biomarkers such as monoaromatic and triaromatic steroids and the saturated hydrocarbon biomarkers are destroyed or diluted with time. The neo-production of adamantanes are also good reaction proxies as well.

Bitumen reactivity in the aqueous environment at temperatures below 300°C seems to be low; however, we have shown that neoformation of compounds such as alkylanthracenes, not abundant in unaltered oils (0 - 3 ppm), at thermal recovery conditions suggests some molecular changes are suitable to monitor steaming effects under current thermal recovery conditions. As an example, figure 3 shows a SAGD produced oil depicting generated methylanthracene (about 10 ppm), compared to a sample upgraded after simulated steam recovery at 350 °C. Alkybenzothiophenes are also produced under SAGD conditions. In general, during simulated thermal recovery experiments the oil asphaltene fraction decreases, but resins do not show such large variations on absolute quantification even though FTMS analysis indicate changes in this fraction are occurring. Furthermore, when hydrous pyrolysis products of two oil sands with different biodegradation levels are compared, the more biodegraded and originally asphaltene enriched sample, generates higher concentration of n-alkanes; however, the production of coke in a reservoir is an issue that has to be further studied in the case of severely biodegraded oils with hydrogen deficits.

The results suggest that the asphaltene fraction is probably the major source of the newly formed saturated and aromatic hydrocarbons, which is consistent with the idea of asphaltene structures rich in aromatic rings interconnected through aliphatic chains and heteroatomic bonds<sup>4-8</sup>. The principal proposed mechanisms are cracking of side chains from aromatic groups and cracking of aliphatic fragments linked through heteroatoms in cyclic systems present in the asphaltene molecular structure. Temperature and heating times are the dominant control factors on hydrocarbon yields as indicated by higher yields with longer heating time and dramatically increasing yields occurring at 350 °C pyrolysis temperature. The amount and properties of hydrocarbons formed during the thermal reactions may also be significantly influenced by the nature and composition of the starting oil which shows very significant variations across the Albertan heavy oil province.

## Conclusions

➤ The results of simulated thermal recovery experiments (under non catalytic steam recovery conditions) suggest that the asphaltene fraction is probably the main source of the newly formed saturated and aromatic hydrocarbons. The principal proposed mechanisms are cracking of side chains from aromatic structures in resins and asphaltenes and cracking of aliphatic fragments linked through heteroatoms in cyclic systems present in the asphaltene molecular structure.

➤ Neof ormation of compounds such as alkylanthracenes at thermal recovery conditions, components absent or not abundant in unaltered oils, suggests some molecular changes are suitable to monitor steaming effects under current thermal recovery procedures. Monitoring of all fluid compositions prior to and during a recovery operation assist in optimizing recovery and reducing costs and are thus recommended.

➤ The results suggest that severely biodegraded oils, with high content of asphaltenes, may have a high potential to be significantly upgraded through very high temperature CSS steam recovery.

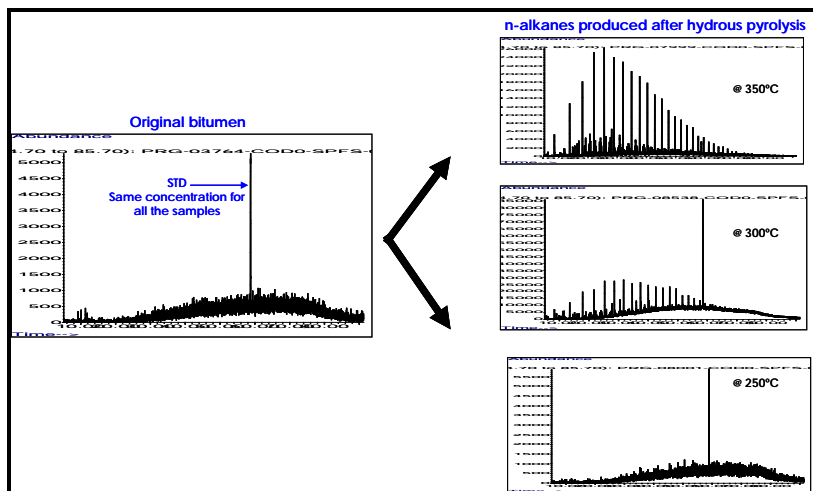
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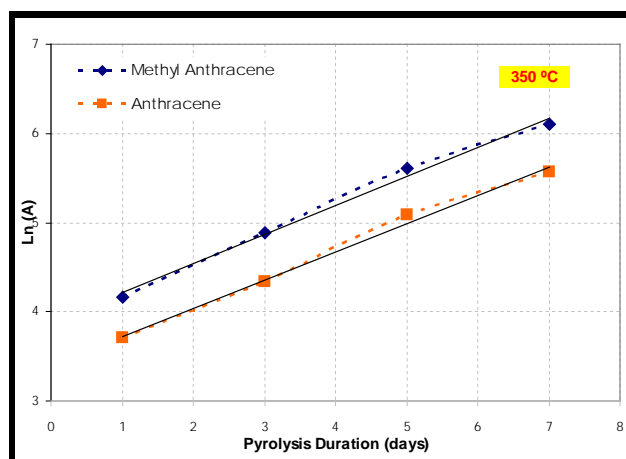
## References

1. Larter, S., Adams, J., Gates, I., Bennett, B., Huang, H., 2006. The origin, prediction and impact of oil viscosity heterogeneity on the production characteristics of tar sand and heavy oil reservoir. Petroleum Society's 7th Canadian International Petroleum Conference. Paper 2006-134.
2. Bennett, B. and Larter, S., 2000. Polar non-hydrocarbon contaminants in reservoir core extracts. *Geochemical Transactions*, **1**(34), pp. 34-37.
3. Bennett, B., Larter, S., Carbognani, L., Pereira, P., 2008. Identification and characterization of reaction proxies for monitoring the progress of thermal processing of heavy oils and tar sands under vis-breaking conditions. *Energy and Fuels*, **22**, pp. 440-448.
4. Strausz, O., Mojelsky, T., and Lown, E., 1992. The molecular structure of asphaltene: an unfolding story. *Fuel*, **71**(12), pp. 1355-1363.
5. Rubinstein, I. and Strausz, O. P., 1979. Thermal treatment of the Athabasca oil sand bitumen and its component parts. *Geochim. Cosmochim. Acta*, **43**(12), pp. 1887-1893.
6. Payzant, J. D., Rubinstein, I., Hogg, A. M. and Strausz, O. P., 1979. Field-ionization mass spectrometry: application to Geochemical analysis *Geochim. Cosmochim. Acta*, **43** (8), pp. 1187-1193.

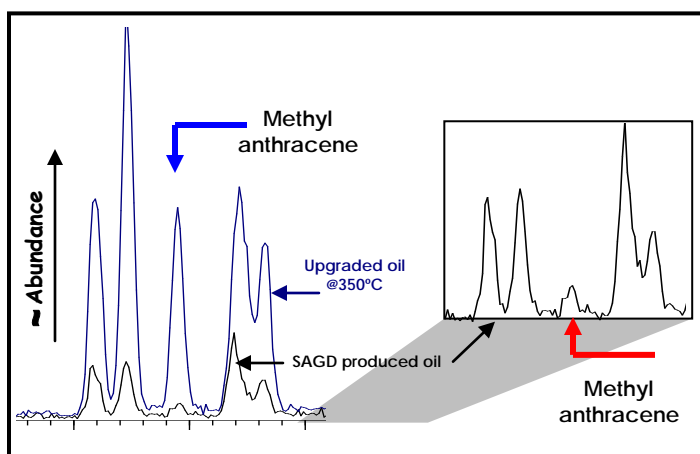
7. Rubinstein, I., Spyckerelle, C. and Strausz, O. P. Pyrolysis of asphaltenes: a source of geochemical information. *Geochim. Cosmochim. Acta* 1979, **43**(1), pp. 1-6.
8. Ignasiak, T. M., Kemp-Jones, A. V. and Strausz, O. P., 1977. The molecular structure of Athabasca asphaltene. Cleavage of the carbon-sulfur bonds by radical ion electron transfer reactions. *J. Org. Chem.*, **42** (2), pp. 312-320.



**Figure 1:** Mass chromatogram m/z 85, depicting the generation of n-alkanes after hydrous pyrolysis @ 300 - 350°C. For most oil sand pools, where n-alkanes have been totally removed by biodegradation, the production of new n-alkanes may allow the monitoring of the progress of the upgrading front in high temperature thermal recovery procedures (>>250°C)



**Figure 2:** Production of methylanthracene and anthracene with time, after up to 7 days of hydrous pyrolysis @ 350°C. Concentration data is calculated using the ion m/z 192 for the methylanthracene and m/z 178 for anthracene. The Ln of the concentration is used to illustrate the apparent first order pseudokinetics of the formation of alkylanthracenes.



**Figure 3:** Mass chromatogram m/z 192, depicting the presence of methyl anthracene in an upgraded oil after hydrous pyrolysis @ 350°C (blue line) and in a SAGD produced oil (black line). The generation of methyl anthracene is lower at SAGD conditions, but the peak is still easily identifiable (see the amplified image of the produced oil, to the right)